

Use of Linearized Versions of Langmuir Model to Study Phosphate Sorption Capacity of Soils

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Abstract — Langmuir model is most commonly used for describing solute sorption in soils. As the Langmuir model is nonlinear, linearized version of it is often used so that model parameters can be obtained by linear regression. Although all the linearized versions of Langmuir model are derived from the same model, there are several limitations. These limitations of using linearized Langmuir equations were studied by fitting phosphorus (P) sorption data collected from five different acid soils of Bangladesh. The sum of squared errors (SSE) and coefficient of determination (R^2) values were used to compare the suitability and applicability of different linearized models. Depending on the SSE and R^2 values, Linearization II best fitted to the data, as reflected by a decrease in SSE values and an increase in R^2 values. On the other hand, Linearization IV had the poorest fit to the P sorption data. The results of this study should promote more critical evaluation of model fits to sorption data and encourage the testing of more sophisticated sorption models.

Keywords - Linearized sorption equations, phosphate sorption maximum, phosphate binding strength, soil, sum of squared errors, coefficient of determination

1. INTRODUCTION

Sorption and desorption pattern of phosphorus (P) in soil controls the transport of this ion to the water bodies. To prepare a sorption isotherm, a known mass of soil is equilibrated with a solution of known concentration of the solute. It is often widely used to study the sorption behavior to soils [1]. The equilibration solute concentration remaining in solution is measured and used to calculate the concentration of ion sorbed to the soil [2]. A sorption model is fitted to the data to obtain sorption parameters for the soil. These sorption parameters are used to estimate parameters such as the sorption capacity of the soil or retardation coefficients to be used in transport modeling. The accuracy of the model parameters will depend on whether the appropriate conceptual model was chosen, whether the experimental

conditions were representative of environmental conditions, and whether an appropriate parameter estimation method was used [1].

Langmuir model is commonly used for describing sorption behavior [3-7]. Four different linearized versions of Langmuir model exists [1] which can be used to obtain directly model parameters by solving the normal equations (i.e., by linear regression). Linear regression is commonly used for obtaining Langmuir sorption parameters because it is convenient, it requires little understanding of the data-fitting process and it is easily done in spreadsheets such as Microsoft Excel [5, 8-14]. The experimental data are required to transform for linearization that results in modifications of error structure, introduction of error into the independent variable, and alteration of the weight placed on each data point [15, 16]. These modifications often lead to differences in fitted parameter values among linear versions of the Langmuir model [3, 4, 6, 17].

The most accurate Langmuir equation will depend on the error structure of the data because a major assumption in regression analyses is that the variance of the errors remains constant. Therefore, if a transformation improves the constancy of the error variance, then the associated linear equation will provide better fits and more accurate parameter estimates than the nonlinear equation [18]. Linearized versions of the Langmuir equation have been shown to provide slightly better parameter estimates than the nonlinear equation when the error variance increases linearly with the dependent variable [19, 20]. The accuracy of the linearized Langmuir equations is still unclear. This is of particular importance in P sorption studies where linearized Langmuir equations are commonly used for obtaining soil sorption parameters [5, 8-14]. Understanding of the linearized Langmuir equations is important in P sorption studies because they are commonly used to obtain important sorption parameters that are used in sustainable agricultural system and safeguarding different environmental niches.

In the present study, sorption data were fitted for different soil series with four linearized versions of the Langmuir equation and later, different versions were

compared by using coefficient of determination (R^2) and sum of squared error (SSE) values. Findings of this research will allow researchers to make more informed decisions when applying the Langmuir model to study P sorption capacity of soil.

2. MATERIALS AND METHODS

Soil sampling and preparation

With a view to study phosphate sorption characteristics of soils, an experiment was conducted in the laboratory of the Department of Soil Science, University of Chittagong, Bangladesh. Five different soil series namely the Borkal (Typic Dystrudepts), the Pahartoli (Aeric Endoaquepts), the Raojan (Aeric Endoaquepts), the Noapara (Typic Endoaquepts) and the Manu (Aeric Dystrudepts) were used in the study. Soil samples at a depth of 0–15 cm were collected and mixed together to form a composite sample. The soils were then air dried at room temperature ($25 \pm 2^\circ\text{C}$) for a week, ground and passed through a 2 mm sieve.

Chemical analysis

The soil samples were analyzed for particle size analysis, pH and organic matter. Bouyoucos hydrometer method was used to determine particle size analysis [21]. The pH of the soil was determined by using a soil to water ratio of 1:2.5. Soil organic carbon was determined by wet oxidation method [22].

Phosphate Sorption Procedures

For sorption study, soil samples (1 g) were equilibrated in a 50 mL centrifuge tube with 25 mL 0.01 M CaCl_2 solution containing 0, 1, 10, 25, 50 and 100 mg (equivalent to 0, 25, 250, 625, 1250 and 2500 mg P kg^{-1} soil) as KH_2PO_4 . The soil samples were then incubated at room temperature ($25 \pm 1^\circ\text{C}$) for 24 hours. This incubation time was chosen in accordance with a previous experiment by Sharpley et al. [23]. The mixtures were centrifuged and the supernatants were analyzed for phosphate following the ascorbic acid blue color method [24]. Phosphorus content was measured by a UV-Vis spectrophotometer (Optima SP-3000 nano, Tokyo, Japan) at 882 nm wavelength. Sorbed P was inferred from the difference between the concentration of soluble P added in the initial solution and the concentration of P in the solution at equilibrium. Each treatment was replicated three times.

Data Analysis:

The Langmuir model, developed for describing the adsorption of gases to a surface is used extensively for describing solute and metal sorption to soils [25]:

$$S = \frac{b_L K_L C}{1 + K_L C} \quad (1)$$

Where S is the concentration of sorbed P (mg kg^{-1}), b_L is the maximum sorption capacity of the soil (mg kg^{-1}), K_L is the Langmuir binding strength coefficient (L kg^{-1}) and C is the equilibrium P concentration in solution (mg L^{-1}).

Sum of the squared errors (SSE):

The Sum of squared errors (SSE) was estimated between observed and calculated values of the dependent variable, in this case the sorbed concentration, S:

$$\text{SSE} = \sum_{i=1}^N w_i [S_i - \hat{S}_i]^2 \quad (2)$$

Where SSE is the objective function to be minimized, N is the number of observations, w_i is the i th weighting factor, S_i is the i th measured value of the dependent variable, and \hat{S}_i is the i th model-predicted value of the dependent variable.

Co-efficient of Determination (R^2):

The coefficient of determination (R^2) measures the contribution of the linear function of independent variables to the variation in dependent variables. Different linearized models of the Langmuir equation (Table 1) were compared by using both the sum of squared errors (SSE) and Co-efficient of determination (R^2) values.

Statistical analysis:

The incubation experiment was arranged in the laboratory according to completely randomized design. Regression curve fitting equations were drawn by the Microsoft Office Excel program. Analysis of variance (ANOVA) was performed by using Minitab statistical software.

3. RESULTS

Physical and chemical properties of Soils

The physical and chemical properties of the studied soils are listed in Table 2. The pH of the soil was acidic in nature with the value ranged from 5.4 to 6.2. The highest and the lowest clay content of the soil were obtained in Manu (40%) and Borkal (30%) soil series, respectively. The organic matter content of the soils was between 1.74 to 2.17%. The organic matter contents of the soils were varied from 1.42 to 2.16% and total P of the same soils varied from 383 to 487 mg kg^{-1} .

Equation comparisons

The P sorption data of the five soil series were plotted according to the four linearized forms the Langmuir model (Table 3 and 4) (Fig. 1 - 4). Linearization II yielded the lowest SSE values in compare to the other four linearized forms of the equation. The SSE values of the five soils ranged from 38-540380 (the Borkal soil series), 13-487024 (the Pahartoli soil series), 122-1250968 (the Raojan soil series), 211- 1315982 (the Noapara soil series) and 13-204806 (the Manu soil series). The highest SSE values were observed in linearization IV. The linearization I and II provided better fits to the data than the other two linearization models, as reflected by the highest co-efficient of determination.

Analysis of variance (ANOVA) showed that significant variation in b_L values were present among the soil series. However, the b_L values obtained from different linearized version of the Langmuir model were not significant statistically. The variations in phosphate binding strength

depending on soil series and different linearized models were also not statistically significant.

Phosphate sorption parameters like phosphate sorption maximum (b_L) and phosphate binding strength (K_L) were estimated from four linearized version of Langmuir models (Table 5). The Borkal soil series had the largest phosphate sorption maximum values in compare to other four soils. Of the four linearization tested, the b_L values ranged from 100-1183 (Borkal series), 634-1027 (Pahartoli series), 873-1000 (Raojan series), 407-1000 (Noapara series) and 537-1000 mg kg⁻¹ (Manu series) with the mean values of 741, 915, 955, 683 and 882 mg kg⁻¹, respectively. On the other hand, the phosphate binding strength values, obtained from different linearized models, varied from 0.1-1.11 (Borkal series), 0.03-0.09 (Pahartoli series), 0.14-0.18 (Raojan series), 0.14-0.67 (Noapara series) and 0.09-2.17 (Manu series), with the mean values of 0.58, 0.05, 0.16, 0.35 and 0.67, respectively.

4. DISCUSSION

Of the four linearizations tested in this study, Linearization I, the linearized form most commonly used in P sorption studies, provided fits to the data, as reflected by a decrease in SSE values and an increase in R^2 values. Linearization II had the highest R^2 values and the lowest SSE values of it indicate the best fits to P sorption data. Different researchers [6, 26, 27]. reported similar sorption parameter values as estimated from the nonlinear Langmuir equation and Linearization 1. Other studies also reported that Linearization IV provides the poorest fits (i.e., highest SSE values) and most dissimilar parameter estimates to the nonlinear equation of all the linearizations [15, 16, 18, 19, 28].

In most of the P sorption related literatures, measurement error was assigned only to the dependent variable and the independent variable was assumed to be error free [15, 18, 20, 28-30]. The assumption of an error-free independent variable may be valid only when the dependent variable of any experiment is directly measured and the independent variable is directly controlled by the experimenter. However, in case of sorption studies, the dependent variable (sorbed concentration) is usually determined from the difference between initial concentrations (the true independent variable) and measurements of the so-called independent variable (equilibrium concentration). Therefore, the assumption of the so-called independent variable being error free is not representative of actual sorption studies.

5. CONCLUSION

Results from the sorption study showed that the linearized versions of the Langmuir equation differ from each other depending on their sum of squared errors (SSE) and coefficient of determination (R^2) values. Among the four versions of Langmuir model, Linearization II yielded the lowest SSE and the highest r^2

values, followed by Linearizations I, III and IV. The results of this study should allow researchers to make more informed decisions when applying the Langmuir model to their sorption data.

5. REFERENCES

- [1] C.H Bolster and G.M. Hornberger, "On the use of linearized langmuir equations", Soil. Sci. Soc. Am. J., 71: 1796-1806, 2007.
- [2] P.S. Nair, T.J. Logan, A.N. Sharpley, L.E. Sommers, M.A. Tabatabai and T.L. Yuan, "Interlaboratory comparison of a standardized phosphorus adsorption procedure", J. Environ. Qual., 3: 591-595, 1984.
- [3] O. Altin, H.O. Ozbelge and T. Dogu, "Use of general purpose adsorption isotherms for heavy metal-clay mineral interactions", J. Colloid Interface Sci., 198: 130-140, 1998.
- [4] S.C. Tsai, and K.W. Juang, "Comparison of linear and nonlinear forms of isotherm models for strontium sorption on a sodium bentonite", J. Radioanal. Nucl. Chem., 243: 741-746, 2000.
- [5] P.J.A. Kleinman and A.N. Sharpley, "Estimating soil phosphorus sorption saturation data from Mehlich-3 data. Commun", Soil Sci. Plant Anal., 33: 1825-1839, 2002.
- [6] K.V. Kumar and S. Sivasenan, "Prediction of optimum sorption isotherm: Comparison of linear and non-linear method", J. Hazard. Mater. B., 126: 198-201, 2005.
- [7] J.J. Wang and D.L. Harrell, "Effect of ammonium and sodium cations and phosphate, nitrate, and chloride anions on zinc sorption and lability in selected acid and calcareous soils", Soil Sci. Soc. Am. J., 69: 1036-1046, 2005.
- [8] A.N. Sharpley, "Dependence of runoff phosphorus on extractable soil phosphorus", J. Environ. Qual., 24: 920-926, 1995.
- [9] K. Borling, E. Otabbong and E. Barberis, "Phosphorus sorption in relation to soil properties in some cultivated Swedish soils", Nutr. Cycling Agroecosyst., 59: 39-46, 2001.
- [10] F.Fang, P.L. Brezonik, D.J. Mulla and L.K. Hatch, "Estimating runoff phosphorus losses from calcareous soils in the Minnesota River basin", J. Environ. Qual., 31: 1918-1929, 2002.
- [11] E.M. D'Angelo, M.V. Vandiviere, W.O. Thom and F. Sikora, "Estimating soil phosphorus requirements and limits from oxalate extract data", J. Environ. Qual., 32: 1082-1088, 2003.
- [12] M.T. Siddique and J.S. Robinson, "Phosphorus sorption and availability in soils amended with animal manures and sewage sludge", J. Environ. Qual., 32: 1114-1121, 2003.
- [13] H. Zhang, J.L. Schroder, J.K. Fuhrman, N.T. Basta, D.E. Storm and M.E. Payton, "Path and multiple regression analyses of phosphorus

- sorption capacity", Soil Sci. Soc. Am. J., 69: 96–106, 2005.
- [14] D. Xu, J. Xu, J. Wu and A. Muhammad, "Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems", Chemosphere, 63: 344–352, 2006.
- [15] J.E. Dowd and D.S. Riggs, "A comparison of estimates of Michaelis–Menten kinetic constants from various linear transformations", J. Biol. Chem., 240: 863–869, 1965.
- [16] R.D. Harter, "Curve-fit errors in Langmuir adsorption maxima", Soil Sci. Soc. Am. J., 48: 749–752, 1984.
- [17] C.P. Schulthess and D.K. Dey, "Estimation of Langmuir constants using linear and nonlinear least squares regression analyses", Soil Sci. Soc. Am. J., 60: 433–442, 1996.
- [18] D., Colquhoun, "A comparison of estimators for a two-parameter hyperbola", J. R. Stat. Soc. Ser. A, 18: 130–140, 1969.
- [19] D., Colquhoun, "Lectures on biostatistics. Clarendon Press, Oxford" 1971.
- [20] G.L. Atkins, and I.A. Nimmo, "A comparison of seven methods for fitting the Michaelis–Menten equation", Biochem. J., 149: 775–777, 1975.
- [21] G.J. Bouyoucos, "The hydrometer as a new method for the mechanical analysis of soils" Soil Sci., 23: 343–35, 1927.
- [22] A., Walkley and I.A. Black, "An Examination of the Degtjareff Method for Determining Soil Organic Matter and a Proposed Modification of the Chromic Acid Titration Method" Soil Sci. 37: 29–38, 1934.
- [23] A.N. Sharpley, L.R. Ahuja, M. Yamamoto and R.G. Menzel, "The kinetics of phosphorus desorption from soil. Soil Sci. Soc. Am. J., 45: 493–496, 1981.
- [24] J. Murphy and H.P. Riley, "A modified single solution method for the determination of phosphate in natural waters", Anal. Chim. Acta., 27: 31–36, 1962.
- [25] I. Langmuir, "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum", J. Am. Chem. Soc., 40: 1361–1402, 1918.
- [26] L.J.A. Gerringa, P.M.J. Herman and T.C.W. Poortvliet, "Comparison of the linear Van den Berg/Ruzic transformation and a non-linear fit of the Langmuir isotherm applied to Cu speciation data in the estuarine environment", Mar. Chem., 48: 131–142, 1995.
- [27] F. Fang, P.L. Brezonik, D.J. Mulla and L.K. Hatch, "Characterization of soil algal bioavailable phosphorus in the Minnesota River basin", Soil Sci. Soc. Am. J., 69: 1016–1025, 2005.
- [28] F. Harrison and S.K. Katti, "Hazards of linearization of Langmuir's model", Chemom. Intell. Lab. Syst., 9: 249–255, 1990.
- [29] P. Persoff and J.F. Thomas, "Estimating Michaelis–Menten or Langmuir isotherm constants by weighted nonlinear least squares", Soil Sci. Soc. Am. J., 52: 886–889, 1988.
- [30] K.H. Houngh and D.Y. Lee, "Comparisons of linear and nonlinear Langmuir and Freundlich curve-fit in the study of Cu, Cd, and Pb adsorption on Taiwan soils", Soil Sci., 163: 115–121, 1998.

Table 1: Different linearized forms of the Langmuir equation. The commonly used name is in parentheses [1].

Equation	Linearized forms	Limitations
Linearization I (Hanes-Woolf)	$\frac{C}{S} = 1/b_L K_L + \frac{C}{b_L}$	Because x (C) and y (C/S) are not independent, the correlation between x and y is overestimated, i.e., equation may provide good fits to data that do not conform to the Langmuir model.
Linearization II (Lineweaver-Burke)	$\frac{1}{S} = \frac{1}{b_L K_L} \cdot \frac{1}{C} + \frac{1}{b_L}$	Transformation leads to clumping of data points near origin—extremely sensitive to variability at low values of S (high values of $1/S$).
Linearization III (Eadie-Hofstee)	$S = b_L - \frac{1}{K_L} \cdot \frac{S}{C}$	Abscissa is not error free; x (S/C) and y (S) data are not independent. In this case, correlation between x and y is underestimated, i.e., equation may provide poor fit to data that do conform to the Langmuir model.
Linearization IV (Scatchard)	$\frac{S}{C} = K_L b_L - K_L S$	x (S) and y (S/C) are not independent. In this case, correlation between x and y is underestimated, i.e., equation may provide poor fit to data that do conform to the Langmuir model.

Table 2: Physical and chemical properties of soils

Soil series	pH	Clay (%)	Organic matter (%)	Total P (mg kg ⁻¹)
Borkal	5.42	30	2.09	383
Pahartoli	5.86	24	1.42	487
Raojan	5.65	38	1.76	375
Noapara	5.45	25	2.16	392
Manu	5.74	24	1.85	456

Table 3: Phosphate sorption equations by using linearized forms of the Langmuir equation

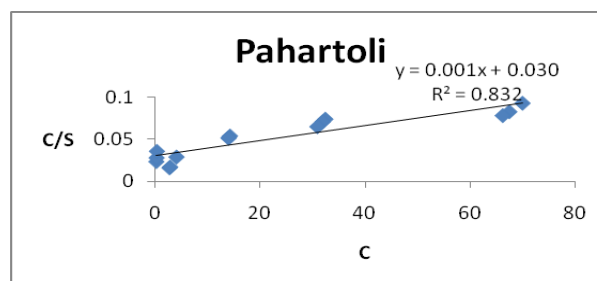
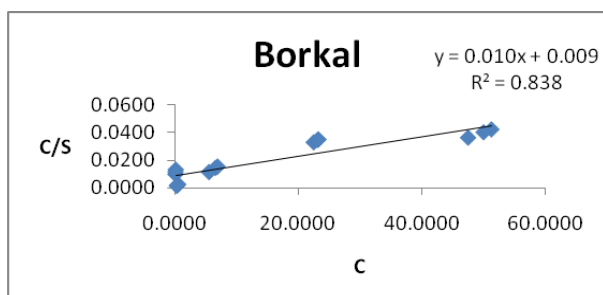
Name of Soil Series	Linearized I	Linearized II	Linearized III	Linearized IV
Borkal	$y = 0.010x + 0.009$	$y = 0.010x - 0.001$	$y = -1.078x + 680.7$	$y = -0.184x + 236.5$
Pahartoli	$y = 0.001x + 0.030$	$y = 0.027x + 0.001$	$y = -11.04x + 663.7$	$y = -0.039x + 40.04$
Raojan	$y = 0.001x + 0.007$	$y = 0.006x + 0.001$	$y = -5.445x + 873.0$	$y = -0.157x + 148.4$
Noapara	$y = 0.001x - 0.007$	$y = 0.003x + 0.002$	$y = -2.608x + 825.2$	$y = -0.216x + 232.1$
Manu	$y = 0.001x + 0.009$	$y = 0.011x + 0.001$	$y = -0.461x + 537.4$	$y = -0.313x + 309.6$

Table 4: Sum of squared errors (SSE) and R² values for the linearized Langmuir equations for five different soils

Name of Soil Series	Linearized I		Linearized II		Linearized III		Linearized IV	
	SSE	R ²	SSE	R ²	SSE	R ²	SSE	R ²
Borkal	4928	0.918	38	0.853	92244	0.20	540380	0.20
Pahartoli	7668	0.592	13	0.996	1754	0.44	487024	0.44

Table 5: Phosphate sorption maximum and phosphate binding strength calculated from different linearized form of the Langmuir equation

Name of Soil Series	Phosphate sorption maximum (b _L)				Phosphate binding strength (k _L)			
	L1	L2	L3	L4	L1	L2	L3	L4
Borkal	100	1000	681	1183	1.11	0.1	0.93	0.18
Pahartoli	1000	1000	634	1027	0.03	0.04	0.09	0.04
Raojan	1000	1000	873	945	0.14	0.17	0.18	0.16
Noapara	1000	500	825	407	0.14	0.67	0.38	0.22
Manu	1000	1000	537	989	0.11	0.08	2.17	0.31



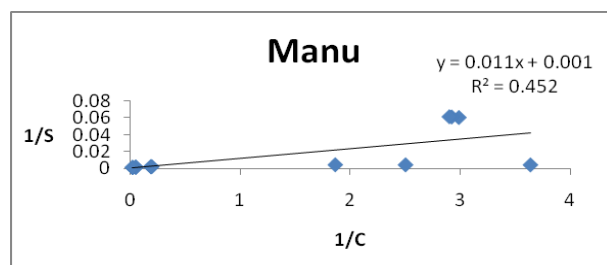
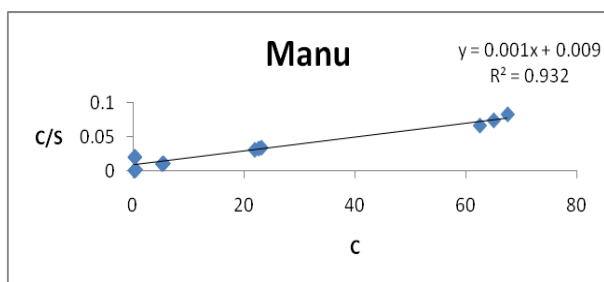
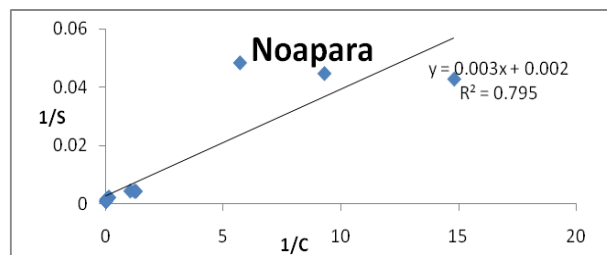
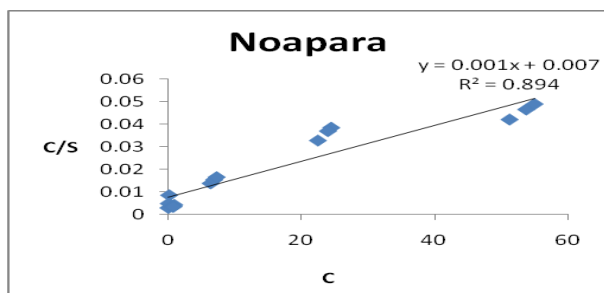
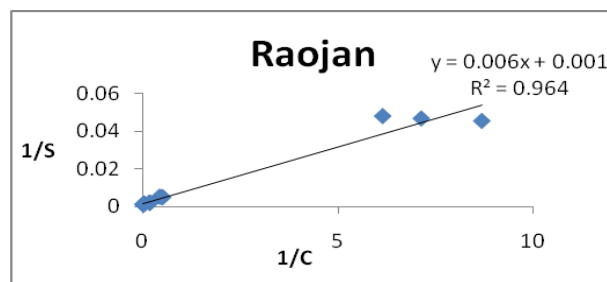
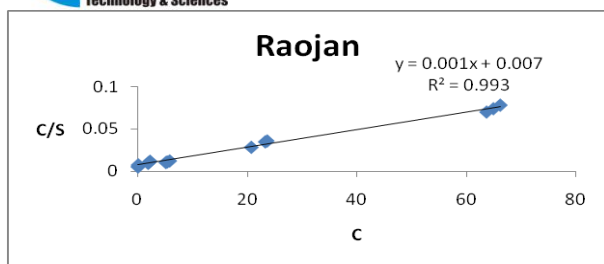
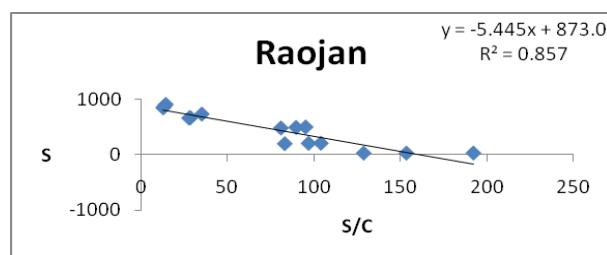
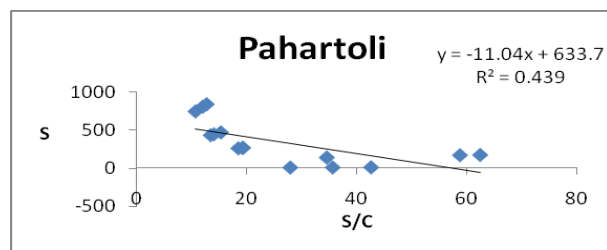
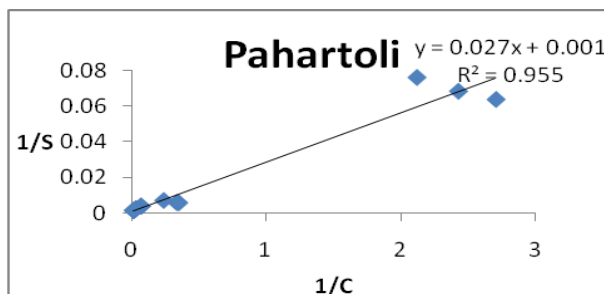
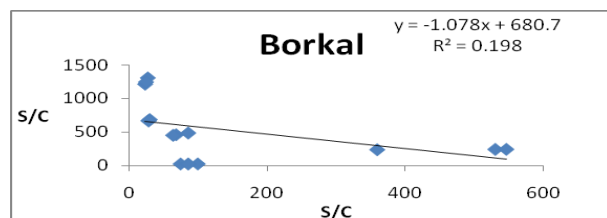
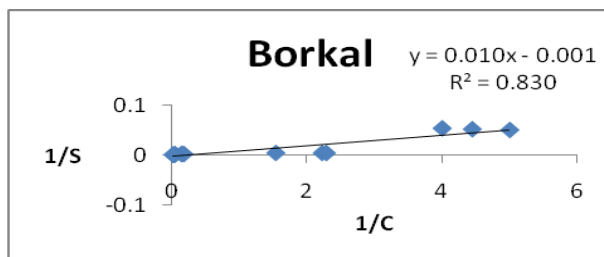


Fig. 1: Phosphate sorption equation of soils fitted by different linearized form of the Langmuir equation (a)
 Linearization-I

Fig. 2: Phosphate sorption equation of soils fitted by different linearized form of the Langmuir equation (b)
 Linearization-II



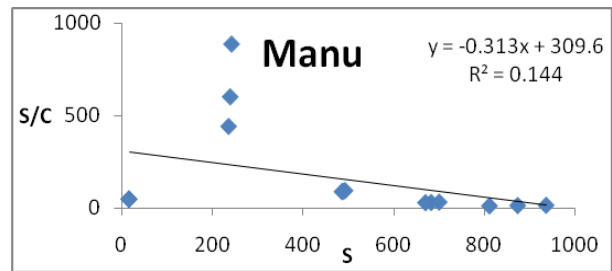
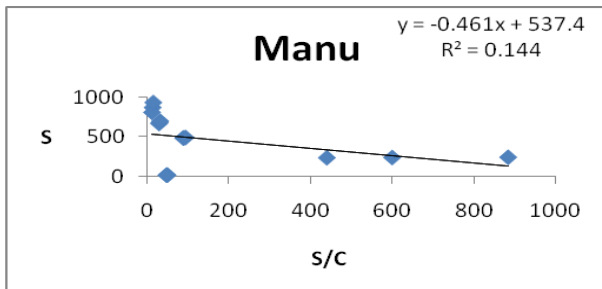
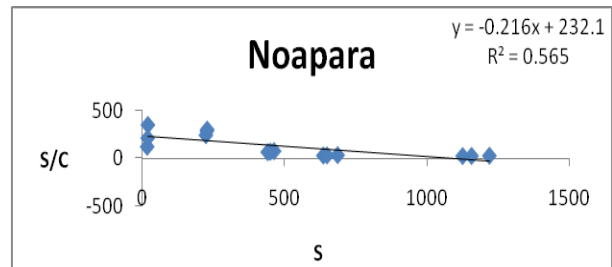
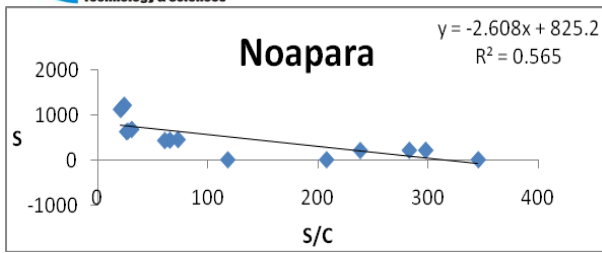


Fig. 3: Phosphate sorption equation of soils fitted by different linearized form of the Langmuir equation (c)
 Linearization-III

Fig. 4: Phosphate sorption equation of soils fitted by different linearized form of the Langmuir equation (d)
 Linearization-IV.

